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THE EFFECT OF TRANSITION METAL OXIDES ON THE STRENGTH, PHASE COMPOSITION, AND MICROSTRUCTURE OF CORDIERITE CERAMICS

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The effect of transition metal oxides and the sintering temperature on the strength parameters of cordierite ceramics synthesized using mechanical activation is investigated. It is established that an introduction of oxide additives improves the strength of ceramics.

The popularity of cordierite as a component for engineering ceramics has been recently growing. Not only pure cordierite products, but also articles based on cordierite with various additives are usually referred to as cordierite ceramics.

Additives of certain oxides introduced in a cordierite mixture contribute to improving the molding, strength, heat-resisting, and other properties of the material [1]. However, the data on this subject are fragmentary.

The purpose of the present work was a systematic study of the effect of simple oxide additives on the strength properties, phase composition, and microstructure of cordierite materials. It follows from some published data [2] that as the charge of the cation introduced to the mixture increases, the strength parameters improve; therefore, the selected additives were oxides with the cation charge ranging from 4+ to 6+ (TiO_2, ZrO_2, V_2O_5, Nb_2O_5, MoO_3, WO_3) in an amount of 10, 20, or 30% (here and elsewhere the molar content is indicated, unless otherwise specified).

Cordierite was synthesized from natural materials: talc $3MgO \cdot 4SiO_2 \cdot H_2O$ (GOST 21234–75), kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (GOST 21288 – 75), gibbsite $Al(OH)_3$ (GOST 11841–76), using preliminary mechanical activation of the mixture of the components taken in the stoichiometric ratio. The chemical reaction in this case is described as follows:

$$4(3MgO \cdot 4SiO_2 \cdot H_2O) + 7(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) + 10Al(OH)_3 = 6(2MgO \cdot 2Al_2O_3 \cdot 5SiO_2) + 33H_2O.$$

After mechanical activation of this mixture in an AGO-3 planetary mill [1] for 5 min and annealing at 1260°C, x-ray phase analysis registered the presence of cordierite in hexagonal syngony.

The samples with oxide additives were prepared as follows. In the first variant, the mixture (talc, kaolinite, and gibbsite) was first activated for 5 min to produce cordierite, then the investigated oxide was added, and mechanical activation was repeated for another 5 min. The activation was performed in an AGO-3 mill with 40*g* acceleration. The total weight of the mill balls of diameter 8 mm was 1.5 kg per drum, and the sample weight per drum was 300 g.

In the second variant, the mixture was prepared by simultaneous activation of all components, i.e., talc, kaolinite, gibbsite, and the considered oxide. The mechanical activation in this case lasted 5 min.

Further investigations established that no significant differences in the strength parameters of samples depending on the mixture preparation variant were registered; therefore, in all subsequent experiments the mixture was prepared in accordance with the second variant, which significantly shortened the time required for this process.

The molding of samples (tablets 18 mm in diameter and 7 mm high) was performed on a hydraulic press at the pressure 40 MPa, holding the sample under loading for 2 min. The plasticizing agent was a mixture of water (75 vol.%) and glycerin (25 vol.%). The plastifier was added in the ratio of 1 g per 3 g powder.

In molding tablets of pure cordierite, about 0.1 g plastifier was squeezed out from the tablet while being under a load. As the oxide content in the samples increased, the mixture became more pliable, and the loss of plastifier under molding reached 0.3 – 0.4 g.

After molding, the samples were dried in the drying cabinet at temperature 200°C for 6 h until the end of weight changes. After drying, the mass of the samples with 10% oxide additive was 3.2 ± 0.1 g, and the samples with 30% oxide additives weighed 3.0 ± 0.05 g, regardless of the type of oxide.

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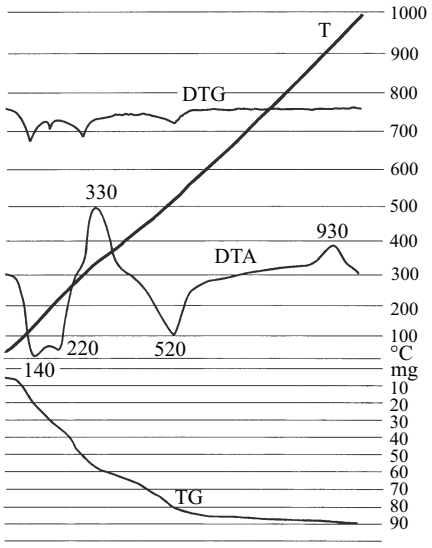

Fig. 1. Derivatogram of cordierite sample with 30% additive of TiO_2.

Next, the samples were annealed at temperature 600°C with the aim of dehydration and dehydroxylation of minerals. Based on the differential thermal analysis data and weighing of samples, weight loss stops at this stage, and under sintering at 1260°C the weight loss is around 0.5% of the initial tablet weight.

It can be seen in Fig. 1 that the endothermic effect at 130 – 150°C is related to the evaporation of water contained in the plasticizer, and the effect at around 220°C is related to dehydroxylation of gibbsite

$$Al(OH)_3 \rightarrow \gamma\text{-}Al_2O_3 + AlOOH,$$

as well as to the transformation of the powder, which had become amorphous under mechanical activation, into the crystalline state. The endothermic effect in the region of 310 – 350°C, in our opinion, is due to burning out of glycerin, since this effect is absent in the pattern of the cordierite mixture without the binding additive. The endothermic effect at 510 – 530°C is related to further dehydroxylation, i.e., the transformation

$$\gamma\text{-}Al_2O_3 + AlOOH \rightarrow \gamma\text{-}Al_2O_3.$$

Another endothermic effect of dehydration of kaolinite occurring in the range of 500 – 700°C is superimposed on the effect specified above. At temperature 850°C the transformation of γ-Al_2O_3 to θ-Al_2O_3 and dehydration of talc are registered:

$$Mg_3Si_4O_{10}(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O.$$

The exothermic effect around 930°C is determined by the modification of the position of oxide ions due to the formation of mullite in the metakaolinite structure [3].

TABLE 1

Additive molar content	Sintering temperature, °C	Compressive strength of samples, MPa	Phase composition
Without additive	1260	90	–
	1340	182	
TiO_2, %:			
10	1260	124	Cordierite
20	1260	317	Cordierite + TiO_2
	1340	340	Cordierite + mullite + TiO_2
30	1260	348	The same
ZrO_2, %:			
10	1260	118	Cordierite + ZrO_2
20	1260	238	The same
	1340	264	Cordierite + zircon + ZrO_2
30	1260	280	Cordierite + mullite + zircon + ZrO_2
V_2O_5, %:			
10	1260	72	Cordierite
20	1260	304	The same
	1340		Not determined
30	1260	425	Cordierite + mullite
Nb_2O_5, %:			
10	1260	94	Cordierite + Nb_2O_5
20	1260	253	Cordierite + mullite + Nb_2O_5
	1340	310	The same
30	1260	293	″
MoO_3, %:			
10	1260	76	Cordierite + MoO_3
20	1260	285	The same
	1340		Not determined
30	1260	–	Cordierite + mullite + MoO_3
WO_3, %:			
10	1260	103	Cordierite + mullite + WO_3
20	1260	294	The same
	1340	330	″
30	1260	320	″

The sample shrinkage in sintering is equal to 23 – 24% for cordierite without oxide additives, 15 – 25% for samples with 10% additives, and 40 – 47% for samples with 20 and 30% additives.

The density of the sintered sample changes in a similar way. The density of samples with 10% additives varies within the same limits as the density of pure cordierite samples and constitutes 1.5 – 1.7 g/cm^3, whereas with the additive content increased to 20 and 30%, the density perceptibly grows and constitutes 2.3 – 2.7 g/cm^3.

The compressive strength of the samples was determined following the GOST 54–58 testing method. The testing was performed on a P-10 hydraulic press (1000 MPa), using a polished metal slab 150 × 150 × 20 mm, and the upper punch.

The data on measuring the strength of ceramics in the presence of oxide additives are given in Table 1. It follows from the above data that with an increasing content of oxide additives, the strength of ceramics grows. The content of the mullite phase increases as well (Fig. 2). The preliminary esti-

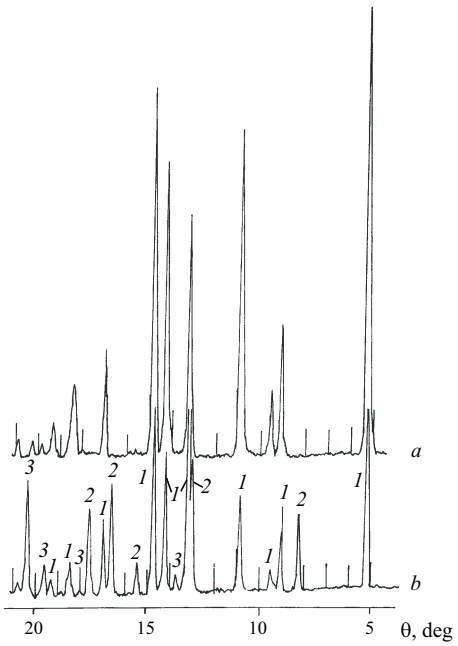

Fig. 2. Diffraction patterns of cordierite samples with TiO_2 additives of 10% (*a*) and 30% (*b*): *1*) cordierite reflections; *2*) mullite reflections; *3*) TiO_2 (rutile) reflections.

mate of the quantitative content of the phases obtained by the method of measuring the prototype samples based on the x-ray phase analysis data indicates that the maximum mullite content can reach 30 wt.%. Thus, oxide additives accelerate the process of mullite crystallization. An elevated sintering temperature (from 1260 to 1340°C) also increases the strength of ceramics on the average by 10 – 15%.

An introduction of oxides modifies the microstructure of ceramics. The scaly material free of oxide additive containing pores up to 10 μm is transformed into a close-grained structure with grains well sintered to each other (Fig. 3). This is presumably the reason for the increased strength of ceramics.

Mullite $3Al_2O_3 \cdot 2SiO_2$ has higher strength parameters than cordierite. At the same time, compared to other materials, mullite has thermal and dielectric constants which are very similar to those of cordierite, and they are chemically compatible. With an increased mullite content, the pore size decreases, whereas the crack resistance, the thermal shock resistance, and the temperature of softening under loading increase [4, 5]. Therefore, the introduction of oxide additives makes it possible to obtain hardened cordierite ceramics

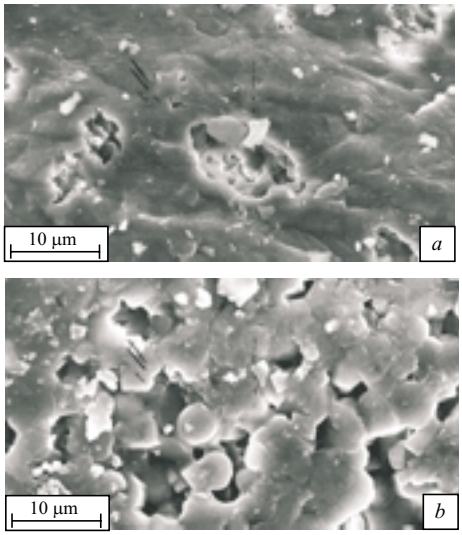

Fig. 3. Microstructure of cordierite ceramics: *a*) cordierite without additive (1340°C, × 1500); *b*) cordierite with 20% additive of TiO_2 (1340°C, × 2200).

No significant distinctions were found in the behavior of oxides depending on the cation charge, they all behave approximately in the same way.

Thus, on adding 20 – 30% oxide additives, the strength of ceramics becomes 3 – 5 times higher, and an increase in the sintering temperature from 1260 to 1340°C increases the strength of ceramics by 10 – 15%.

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